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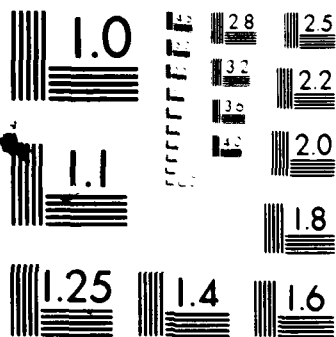
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# PREPARATION AND PURIFICATION OF HMX AND RDX INTERMEDIATES (TAX AND SEX)

## SECOND PHASE FINAL REPORT

C.D. Bedford  
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>This final report describes the feasibility of preparing 4 kg of 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX). The objectives were to (1) establish the technical feasibility of producing amounts of SEX needed for toxicological testing (about 4 kg), (2) provide this material in satisfactory purity and with proper analytical characterization of residual impurities, and (3) provide a cost-plus-fixed-fee estimate for preparation of the compound. → next page |                                     |   |

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19. KEY WORDS (Continued)

20 ABSTRACT (Continued)

SEX was prepared by nitrolysis of 1,5-diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine (DADN), using a mixture of trifluoroacetic anhydride and 100% nitric acid. The crude SEX was contaminated with 50% of DADN, HMX, or of a mixture of both, depending on the reaction conditions.

Analytically pure SEX (99.9+%) was obtained through the following procedure. Open hot column chromatography (90-100°C) on silica gel with a nitromethane eluent was used to remove the 5 to 20% DADN contamination. The resulting SEX/HMX mixture was separated to yield 99.+% SEX by preparative high-pressure liquid chromatography (HPLC) on prepacked silica gel columns, again using a nitromethane eluent. Conditions for the preparation of the DADN/SEX/HMX mixture have been optimized and the process can be conducted batchwise. Thus, SEX can be provided in the quantities desired for subsequent purification.

Determination of the shock sensitivity of SEX showed that it can sustain greater than 300 kg-cm in a drop weight test (compared with 148 kg-cm for pure HMX). However, SEX is sensitive to direct, strong hammer blows and therefore must be treated as an explosive material in handling and shipping.

## SUMMARY

This final report describes the feasibility of preparing 4 kg of 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX). The objectives were to (1) establish the technical feasibility of producing amounts of SEX needed for toxicological testing (about 4 kg), (2) provide this material in satisfactory purity and with proper analytical characterization of residual impurities, and (3) provide a cost-plus-fixed-fee estimate for preparation of the compound.

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A cost estimate for preparation of 4 kg of SEX in the purity needed for toxicological studies is being submitted separately.

FOREWORD

Citations of trade names in this report does not constitute an official endorsement or approval of the use of such items.

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## GLOSSARY

DADN - 1,5-Diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine

FEP - Fluorinated ethylene-propylene polymer

HMX - 1,3,5,7-Tetranitro-1,3,5,7-tetrazocine

HPLC - High-pressure liquid chromatography

NMR - Nuclear magnetic resonance

RDX - 1,3,5-Trinitro-1,3,5-triazine

SEX - 1-Acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine

TAT - 1,3,5,7-Tetraacetyloctahydro-1,3,5,7-tetrazocine

TAX - 1-Acetylhexahydro-3,5-dinitro-1,3,5-triazine

TFAA - Trifluoroacetic anhydride

TLC - Thin layer chromatography

## INTRODUCTION

The U.S. Army Medical Research and Development Command is interested in determining the potential environmental and health hazards of wastewaters containing SEX and TAX. SEX and TAX are unavoidable coproducts formed during the manufacturing of RDX/HMX. In 1977, 34,000 pounds of HMX were produced, or about 123 pounds per day. At full production levels, more than 1000 pounds of SEX and 3600 pounds of TAX per day could be generated and discharged. The wastewaters from the manufacturing of RDX/HMX are subject to environmental discharge limitations established by regulatory agencies. Evaluation of the potential hazards of these wastewaters to the environment is a necessary portion of the data base needed to estimate environmental hazards. Because the wastewaters will contain large amounts of both SEX and TAX, it is important to obtain sufficient quantities of pure SEX and TAX for a complete toxicological investigation.

Since SEX is of no value as an explosive, little effort has been directed to its deliberate synthesis. Therefore, we investigated the feasibility of preparing 4 kg of SEX in the purity (> 98%) necessary for these studies. Our specific objectives were:

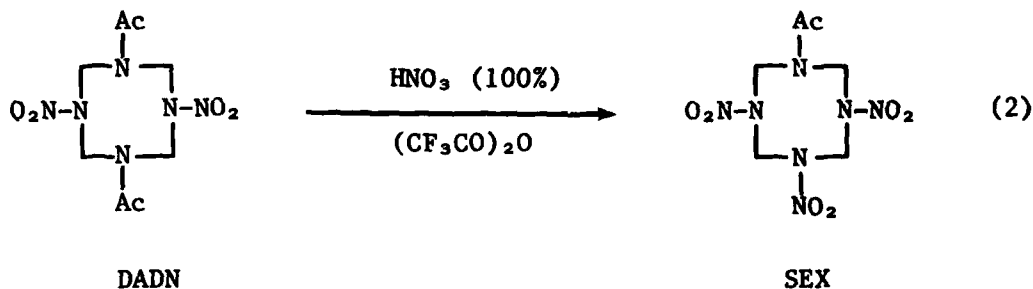
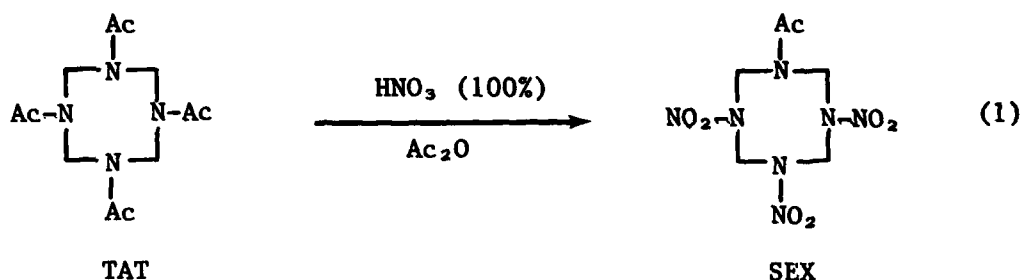
- (1) Investigate the most promising methods reported for the preparation of SEX and verify successful syntheses on a 50-g batch scale.
- (2) Investigate both known and alternative purification methods for SEX to determine which is the most effective.
- (3) Determine the most efficient methodology for the analysis of SEX.
- (4) Further characterize SEX by determining its shock sensitivity, to permit classification for shipping, handling, and storing.

- (5) Prepare a final report fully documenting the information obtained from the study and including a best-efforts cost estimate for the production of the required quantity of SEX.

Our efforts to prepare and characterize SEX are described in the following sections. The preparation and purification of TAX is described elsewhere.<sup>1</sup>

# PREPARATION OF SEX

SEX was prepared according to two methods of Gilbert,<sup>2</sup> as shown in Equations (1) and (2).



Treatment of 2.0 g (7 mmole) of TAT with 100% nitric acid/acetic anhydride mixture yielded 93% and 40% of crude SEX in separate experiments. Based on proton NMR and TLC analysis, the crude SEX proved to be a mixture of DADN, SEX, and HFX in a ratio of approximately 0.5:1:1. The variable yield, coupled with difficult methods for the preparation of TAT and the separation of SEX from contaminants, made this route, shown in Equation (1), inadequate for large-scale preparation.

SEX was then prepared from DADN<sup>3</sup> as shown in Equation (2). Treatment of up to 40 g (0.2 mole) of DADN with 100% nitric acid/trifluoroacetic anhydride mixtures consistently yielded 60% to 75% of crude SEX, as listed in Table 1. The reaction between DADN and the nitrolyzing medium, 100% HNO<sub>3</sub>/TFAA, was modified slightly from that followed in the preparation of TAX.<sup>1</sup> The DADN was found to be insoluble in TFAA and had to be dissolved in the nitric acid before mixing. Furthermore, when the DADN and the nitrolyzing medium were allowed to stand at room temperature for prolonged periods, no exotherm was observed, such as occurred during the preparation of TAX.

The synthesis, although successful, had two serious drawbacks: (1) the amount of TFAA used in the originally designed reaction procedure represented a substantial cost, making the preparation of 4-kg quantities of SEX prohibitively expensive, and (2) the crude SEX was contaminated with both HMX and DADN, which could not be readily removed by physical separation methods such as column chromatography, recrystallization, or extraction.

#### Reaction Conditions

Because of the insolubility of DADN, and to simplify the purification of SEX, we wished to produce a mixture low in DADN. This can be accomplished at the expense of higher conversions to HMX. We varied time (10 min to 5 hr), temperature (35° to 50°C), and equivalents of N<sub>2</sub>O<sub>5</sub> (1 to 25), as determined by the added amount of trifluoroacetic anhydride, to determine conditions that result in: (a) crude yield  $\geq$  70%, (b) DADN  $\leq$  20%, and (c) maximum SEX/HMX ratio. For comparison, we have chosen an approximate product composition of 10/50/40, DADN/SEX/HMX, as a standard (as determined by proton NMR).

Various sets of conditions result in the desired product mixture. Time, temperature and equivalents of N<sub>2</sub>O<sub>5</sub> are interrelated variables. Any one of these three variables may be used as the stress that provides the desired results. Any two of them may be kept low, if the third is high. For example, the standard product mixture (10/50/40, DADN/SEX/HMX)

Table 1  
CONDITIONS FOR CRUDE SEX PREPARATION

| Run  | Na <sub>2</sub> O <sub>3</sub><br>eq. | TFAA<br>(ml) | Temp.<br>(°C) | Time<br>(min.) | Yield <sup>a</sup> |      | Composition <sup>b</sup> |            |            |
|------|---------------------------------------|--------------|---------------|----------------|--------------------|------|--------------------------|------------|------------|
|      |                                       |              |               |                | (g)                | (%)  | DADN<br>(%)              | SEX<br>(%) | MAX<br>(%) |
| 1    | 25                                    | 18           | 25            | 45             | 1.10               | 73.8 | 40                       | 40         | 20         |
| 2    | 25                                    | 18           | 25            | 90             | 1.13               | 75.8 | 20                       | 40         | 40         |
| 3-1  | 25                                    | 18           | 33            | 30             | 0.90               | 60.4 | 20                       | 60         | 20         |
| -2   |                                       |              |               | 45             |                    |      | Trace                    | 60         | 40         |
| 4-1  | 12.5                                  | 8.8          | 38            | 15             | 0.95               | 63.8 | 20                       | 60         | 20         |
| -2   |                                       |              |               | 30             |                    |      | -                        | 50         | 50         |
| -3   |                                       |              |               | 45             |                    |      | -                        | 60         | 40         |
| 5-1  | 25                                    | 18           | 5             | 15             | 1.45               | 97.0 | 100                      | -          | -          |
| -2   |                                       |              |               | 30             |                    |      | 100                      | -          | -          |
| -3   |                                       |              |               | 45             |                    |      | 100                      | -          | -          |
| -4   |                                       |              |               | 90             |                    |      | 95                       | Trace      | Trace      |
| 6-1  | 2                                     | 1.4          | 35            | 10             | 1.14               | 75.0 | 100                      | -          | -          |
| -2   |                                       |              |               | 20             |                    |      | -                        | -          | -          |
| -3   |                                       |              |               | 30             |                    |      | -                        | -          | -          |
| -4   |                                       |              |               | 40             |                    |      | -                        | -          | -          |
| -5   |                                       |              |               | 50             |                    |      | 75                       | 25         | -          |
| 7-1  | 2                                     | 1.4          | 35            | 50             | 1.04               | 69.0 | 75                       | 25         | -          |
| -2   |                                       |              |               | 80             |                    |      | 48                       | 46         | 6          |
| -3   |                                       |              |               | 110            |                    |      | 37                       | 45         | 18         |
| -4   |                                       |              |               | 140            |                    |      | 13                       | 52         | 35         |
| 8-1  | 1                                     | 0.7          | 35            | 80             | 0.89               | 60.0 | 65                       | 33         | -          |
| -2   |                                       |              |               | 110            |                    |      | -                        | -          | -          |
| -3   |                                       |              |               | 140            |                    |      | 35                       | 48         | 17         |
| -4   |                                       |              |               | 170            |                    |      | 22                       | 56         | 22         |
| -5   |                                       |              |               | 230            |                    |      | 14                       | 51         | 32         |
| 9-1  | 3                                     | 2.1          | 34            | 30             | 0.94               | 62.0 | -                        | -          | -          |
| -2   |                                       |              |               | 60             |                    |      | 59                       | 33         | 7          |
| -3   |                                       |              |               | 120            |                    |      | 31                       | 49         | 21         |
| -4   |                                       |              |               | 150            |                    |      | 18                       | 55         | 27         |
| -5   |                                       |              |               | 180            |                    |      | 11                       | 56         | 28         |
| 10   | 2                                     | 1.4          | 35            | 80             | 1.10               | 74.0 | 50                       | 50         | Trace      |
| 11   | 2                                     | 7.0          | 35            | 300            | 7.4                | 71.0 | 12                       | 55         | 33         |
| 12-1 | 2                                     | 2.8          | 42            | 30             | 1.50               | 50.0 | 36                       | 47         | 17         |
| -2   |                                       |              |               | 60             |                    |      | 30                       | 51         | 19         |
| -3   |                                       |              |               | 90             |                    |      | 7                        | 66         | 27         |
| -4   |                                       |              |               | 120            |                    |      | 12                       | 59         | 29         |
| 13-3 | 2                                     | 2.8          | 47            | 60             | -                  | -    | 12                       | 55         | 33         |
| -4   |                                       |              |               | 120            | -                  | -    | -                        | 10         | 90         |
| 14   | 2                                     | 2.8          | 50            | 60             | 0.80               | 27.0 | -                        | 33         | 66         |
| 15   | 2                                     | 2.8          | 50            | 70             | 1.00               | 33.0 | -                        | 50         | 50         |
| 16-1 | 3                                     | 4.2          | 45            | 50             | 2.10               | 69.0 | 20                       | 45         | 35         |
| -2   |                                       |              |               | 60             |                    |      | 5                        | 52         | 43         |
| -3   |                                       |              |               | 75             |                    |      | -                        | 34         | 66         |
| 17-1 | 4                                     | 5.6          | 40            | 40             | 2.00               | 66.0 | 25                       | 40         | 35         |
| -2   |                                       |              |               | 60             |                    |      | 5                        | 55         | 40         |
| -3   |                                       |              |               | 75             |                    |      | -                        | 45         | 55         |
| 18-1 | 4                                     | 5.6          | 45            | 15             | 2.30               | 79.0 | 46                       | 27         | 27         |
| -2   |                                       |              |               | 30             |                    |      | 18                       | 53         | 30         |
| -3   |                                       |              |               | 45             |                    |      | 1                        | 56         | 43         |
| 19-1 | 5                                     | 7.0          | 35            | 60             | -                  | -    | 10                       | 60         | 30         |
| -2   |                                       |              |               | 120            |                    |      | -                        | 50         | 50         |
| -3   |                                       |              |               | 180            |                    |      | -                        | 40         | 60         |
| 20   | 5                                     | 7.0          | 35            | 60             | 2.30               | 76.0 | 11                       | 58         | 32         |
| 21-1 | 5                                     | 7.0          | 40            | 15             | 2.60               | 89.0 | 48                       | 46         | 6          |
| -2   |                                       |              |               | 30             |                    |      | 15                       | 64         | 21         |
| -3   |                                       |              |               | 45             |                    |      | 2                        | 64         | 34         |
| 22-1 | 5                                     | 7.0          | 45            | 15             | 2.30               | 78.0 | 22                       | 52         | 26         |
| -2   |                                       |              |               | 30             |                    |      | 2                        | 49         | 49         |
| -3   |                                       |              |               | 45             |                    |      | -                        | 25         | 75         |
| 23-1 | 5                                     | 7.0          | 50            | 10             | 2.10               | 71.0 | 14                       | 57         | 29         |
| -2   |                                       |              |               | 25             |                    |      | -                        | 30         | 70         |
| 24   | 8                                     | 11.2         | 35            | 30             | -                  | -    | 10                       | 60         | 30         |

:       **Note:** All runs, except number 11, used 3.0 g DADN and 20 ml HNO<sub>3</sub>.

:       **a)** Crude Product; the sum of all samples in the run.

**b)** Composition determined by proton NMR, with a possible deviation of  
          +5% on each of three components.

is obtained under each of the following conditions:

|   | <u>Equivalents <math>N_2O_5</math></u> | <u>Temperature, <math>^{\circ}C</math></u> | <u>Time</u> | <u>Run #</u> |
|---|--|--|-------------|--------------|
| : | 2                                      | 35   | 5 hr        | 11           |
| : | 2                                      | 50   | 60 min      | 13-3         |
|   | 8                                      | 35   | 30 min      | 24           |

Optimum conditions will require compromise. Because trifluoroacetic anhydride is expensive, a low number of  $N_2O_5$  equivalents is more economic. A low operating temperature is safer and introduces fewer problems associated with gas evolution. A shorter time is more convenient and determines the type of reactor most desirable and, in turn, the scale of reaction that may be run safely.

Results are summarized in Table 1. Conditions that produced a mixture of  $\sim 10/50/40$ , DADN/SEX/HMX are plotted in Figure 1. Some data points are made by extrapolation.

In choosing among several sets of conditions that will achieve a given product mixture, the overall yield must also be considered. Runs Nos. 12 through 15, using two equivalents of  $N_2O_5$  at temperatures above  $35^{\circ}C$ , resulted in lower yields ( $\sim 50\%$ ) than those produced under other conditions.

The optimum conditions selected and demonstrated on a 40-g quantity of DADN (see Experimental Procedure section) were 1-hour reaction time at  $40^{\circ}C$  and 4 equivalents of  $N_2O_5$ . Scale-up to kilogram quantities of DADN should not present difficulties since no exotherm is observed when DADN and the nitrolyzing medium were allowed to stand at room temperature for a prolonged period or when heated to  $50^{\circ}C$ .

#### TFAA Cost

As runs 1 through 5 in Table 1 indicate, the quantities of TFAA required for the preparation of 4-kg SEX represent a substantial cost (at \$15 per pound). We found that 4 equivalents of TFAA (relative to the amount of DADN used) had little effect on the yield or purity of SEX



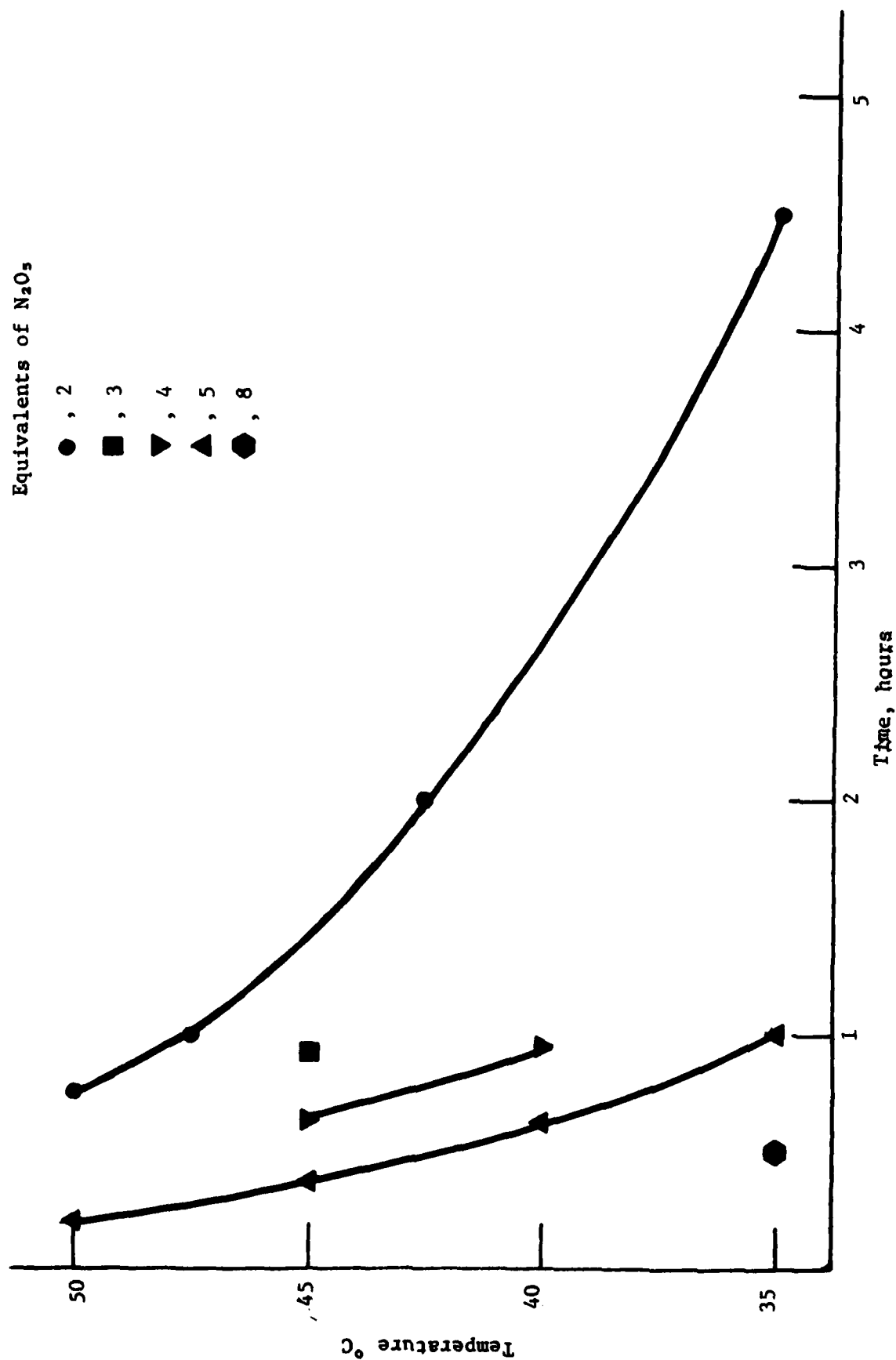


FIGURE 1. TIME, TEMPERATURE AND EQUIVALENTS OF  $N_2O_5$  REQUIRED TO OBTAIN A 10/50/40-DADN/SEX/HMX MIXTURE (As determined by proton NMR).

(see Table 1). Since the reaction conditions require that DADN be dissolved in  $\text{HNO}_3$  (100%) before mixing with the anhydride, we see no need to use greater than 4 equivalents of TFAA for the reaction. Thus, the conditions we have developed for the preparation of a 4-kg quantity of SEX offer a substantial savings in TFAA cost compared to the initial process.

## PURIFICATION OF SEX

The crude SEX obtained by the method described above contained a minimum of 40% contamination of DADN or HMX, or both, in variable amounts (Table 1). Solubility, crystallization, extraction, complexation and chromatography were explored as potential purification methods. This effort culminated in an effective purification procedure requiring two successive chromatographic separations. The first, hot column chromatography of the DADN/SEX/HMX mixture, removed all traces of DADN. The second, chromatography by preparative HPLC, separates SEX and HMX, yielding 99+% purity SEX.

### Solubility

From initial experiments, we determined that the major problem in the DADN/SEX/HMX product mixture was solubility. The relative solubility of the three components is  $DADN < SEX < HMX$ . Therefore, we examined the solubility of DADN under a variety of conditions and solvents, since it is the most insoluble component of the mixture, and its removal would substantially increase the solubility of the remaining two components. The solvents used in these experiments are listed below. In 10 ml of each solvent was placed 0.5 g of DADN, and the mixtures were stirred at ambient temperature for 8 hours. Since DADN did not dissolve in any of the solvents, the mixtures were heated to 50-55°C and stirred for an additional 6 hours. Since the DADN still did not dissolve, an additional 10 ml of solvent was added to each test tube, and stirring was continued at room temperature for 8 hours. Finally each test tube was heated again to 50-60°C and stirred for an additional 6 hours. DADN was found to be soluble in 20 ml of dimethyl sulfoxide (DMSO) at room temperature. Because of the poor solubility of DADN, we decided to run the nitration reactions of (DADN+SEX) for longer periods, to ensure minimum DADN contamination of the final product mixture. We found that a smaller amount of DADN

in the mixture increased the overall solubility of the mixture. In turn, the increased solubility made it easier to apply the mixture onto a gravity-fed chromatographic column, thus enhancing the possibility of obtaining purified SEX.

#### SOLVENTS USED FOR SOLUBILITY TESTS ON DADN

|                    |                          |
|--------------------|--------------------------|
| Acetic acid        | Methanol                 |
| Acetic anhydride   | 1-Methyl-2-pyrrolidinone |
| Acetone            | 2-Methoxyethyl ether     |
| Acetonitrile       | Methyl ethyl ketone      |
| Aminoethanol       | Nitrobenzene             |
| 4-Butyrolactone    | Nitromethane             |
| Cyclohexanone      | 2,4-Pentanedione         |
| Diethylene glycol  | Pyridine                 |
| Dimethyl formamide | Sulfolane                |
| Dimethyl sulfoxide | Triethyl amine           |
| Ethyl acetate      | Triethylene glycol       |
| Formamide          | Water                    |

#### Extraction

The low solubility of the crude SEX indicated that purification might be achieved by soxhlet extraction. Extraction with a variety of solvents on crude DADN/SEX/HMX mixtures, listed in Table 2, showed that minor improvements could be made in the purity of SEX. On the basis of the results shown in Table 2, ethyl acetate was selected as the solvent for partial purification of SEX. It was evident from runs 3, 8, 9, and 10 that HMX and SEX can be partially removed from the crude reaction mixture.

The problem of HMX contamination of the extracted SEX can be minimized by running the initial reaction for only a short time (see run 10, Table 1). Ethyl acetate extraction of a mixture containing predominately DADN and SEX (run 10, Table 2) indicates that the purity of SEX can be increased by approximately 30%. Two major drawbacks still exist:

Table 2  
SOXHLET EXTRACTION OF CRUDE DADN/SEX/HMX MIXTURES

| Run  | Solvent                         | Quantity<br>(ml) | Weight<br>Extracted<br>(g) | Time<br>(hr) | DADN          | SEX           | HMX        |
|------|---------------------------------|------------------|----------------------------|--------------|---------------|---------------|------------|
| 1    | Acetone <sup>a</sup>            | 150              | 0.84                       | 16           | 40            | 40            | 20         |
| 2    | Methylethyl ketone <sup>a</sup> | 150              | 0.51                       | 16           | 30            | 60            | 10         |
| 3    | Ethyl acetate <sup>a</sup>      | 150              | 0.21                       | 16           | -             | 28            | 72         |
| 4    | Tetrahydrofuran <sup>b</sup>    | 130              | 0.26                       | 15           | Trace<br>(14) | Trace<br>(68) | 99<br>(18) |
| 5    | 1,2-Dichloroethane <sup>b</sup> | 200              | 0.07                       | 15           | 4             | 72            | 24         |
| 6    | Dioxane <sup>b</sup>            | 200              | 0.22                       | 15           | 20            | 64            | 16         |
| 7    | Ethanol <sup>b</sup>            | 130              | -                          | 15           | -             | -             | -          |
| 8-1  | Ethyl acetate <sup>b</sup>      | 150              | 0.13                       | 2            | -             | -             | 100        |
| -2   |                                 |                  | 0.17                       | 4            | -             | Trace         | 99         |
| -3   |                                 |                  | 0.30                       | 8            | -             | 50            | 50         |
| -4   |                                 |                  | 0.44                       | 27           | Trace<br>(21) | 50<br>(65)    | 50<br>(14) |
| 9    | Ethyl acetate <sup>c</sup>      | 250              | 1.04                       | 48           | Trace         | 50            | 50         |
| 10-1 | Ethyl acetate <sup>d</sup>      | 250              | 0.19                       | 18           | 17            | 83            | -          |
| -2   |                                 |                  | 0.10                       | 36           | 24            | 76            | -          |

Note: The composition of all materials and residues in the table is determined by proton NMR.

<sup>a</sup>The initial 1.0 g of mixture consisted of a 50/33/17 ratio of DADN/SEX/HMX.

<sup>b</sup>The initial 0.5 to 1.0 g of mixture consisted of an 8/52/40 ratio of DADN/SEX/HMX.

<sup>c</sup>The initial 3.0 g of mixture consisted of a 15/60/25 ratio of DADN/SEX/HMX.

<sup>d</sup>The initial 1.0 g of mixture consisted of a 60/40/trace ratio of DADN/SEX/HMX.

(1) the SEX is still contaminated by approximately 20% to 25% DADN, and  
(2) the recovery of SEX is very low, approximately 20% to 40%. Although  
the remaining DADN/SEX mixture can be recycled, this possibility is  
somewhat tenuous because HMX may form from the remaining unextracted SEX.  
Ethyl acetate will preferentially extract HMX from a DADN/SEX/HMX mixture,  
thus introducing this undesired contaminant. These results indicate that  
the highest purity SEX to be obtained by extraction is approximately  
80%.

It is postulated that cocrystallization of DADN, SEX, and HMX precludes further purification of SEX by extraction with ethyl acetate. Furthermore, the cocrystallization of these three components precludes the use of centrifugation as a method of separation, with results similar to those observed in the TAX case.<sup>1</sup>

#### Crystallization<sup>4</sup> and Complexation

Recrystallization was first attempted on HMX/SEX/DADN mixtures. We postulated that in these mixtures DADN would precipitate preferentially because of its low solubility, discussed above. This was not the case. The rapid precipitation of DADN from the solvent systems affords nucleation sites for both SEX and HMX. This precipitation accounts for the observed low purity of SEX in samples containing quantities of DADN, as shown in Table 3, runs 1 through 4, and for the poor results encountered during extraction experiments. Table 3, runs 5 through 7, show that substantial improvement in the SEX purity can be obtained by recrystallization from nitromethane after removal of DADN by hot column chromatography, discussed below. Thus, when 200 mg of a 90/10 mixture of SEX/HMX was recrystallized, 90 mg (45% recovery) of 98+% SEX was obtained. In run 6, a 61/39 mixture of SEX/HMX was recrystallized once to yield a 75/25 SEX/HMX mixture with 85% recovery of material. However, despite the solvent used, the SEX remained contaminated with varying amounts of HMX. In addition to the lack of separation by crystallization, the amounts of solvents required to dissolve the mixture of compounds made recrystallization inappropriate.

Table 3

## RECRYSTALLIZATION OF CRUDE SEX

| Run              | Wt.<br>(g) | Ratio of Products |     |     | Solvent      | Recovery<br>(g) | Ratio of Products<br>Recrystallized <sup>a</sup> |      |      |
|------------------|------------|-------------------|-----|-----|--------------|-----------------|--|------|------|
|                  |            | DADN              | SEX | HMX |              |                 | DADN   | SEX  | HMX  |
| 1                | 1.0        | 15                | 40  | 45  | Acetone      | 0.83            | b  | b    | b    |
| 2                | 1.0        | 15                | 40  | 45  | Acetonitrile | 0.90            | b  | b    | b    |
| 3                | 0.5        | 5                 | 65  | 30  | Nitromethane | 0.19            | b  | b    | b    |
| 4                | 0.5        | 5                 | 65  | 30  | Nitromethane | 0.25            | b  | b    | b    |
| 5                | 0.2        | -                 | 90  | 10  | Nitromethane | 0.044           | -  | 98.6 | 1.4  |
|                  |            |                   |     |     |              |                 | -  | 98.6 | 1.4  |
| 6-1 <sup>c</sup> | 3.7        | -                 | 61  | 39  | Nitromethane | 1.74            | -  | 75   | 25   |
| -2 <sup>c</sup>  |            |                   |     |     |              | 1.43            | -  | 50.3 | 49.7 |
| 7-1 <sup>c</sup> | 0.8        | -                 | 90  | 10  | Nitromethane | 0.29            | -  | 94   | 6    |
| -2 <sup>c</sup>  |            |                   |     |     |              | 0.11            | -  | 86.5 | 13.5 |

<sup>a</sup> Composition determined by either proton NMR or analytical HPLC.<sup>b</sup> All three components were present as determined by TLC.<sup>c</sup> Second crop isolated from recrystallization of crude SEX.

The failure to purify SEX by recrystallization prompted an examination of complexation as a purification technique. HMX is known to form complexes with numerous ketones,<sup>5,6</sup> amides,<sup>7</sup> and aromatic substrates.<sup>8</sup> We postulated that HMX complexes would sufficiently alter the solubility of HMX relative to the SEX/HMX or DADN/SEX/HMX mixtures to allow preferential precipitation of SEX or DADN/SEX. However, recrystallization of DADN/SEX/HMX mixtures from nitromethane/cyclohexanone (cyclohexanone complexes with HMX<sup>5,6</sup>) yielded mixtures still contaminated with HMX, as shown in Table 4, runs 1 and 2.

When SEX/HMX mixtures were employed (DADN removed by hot column chromatography on silica gel, discussed below) a significant increase in the SEX purity was observed upon recrystallization from a 1:1 nitromethane/cyclohexanone mixture. Thus, 0.75 g of a 58/42% SEX/HMX mixture yielded 0.51 g (68% recovery) of 93/7% SEX/HMX product (Table 4, run 4). A 1:1 mixture of dimethylformamide/nitromethane favored preferential precipitation of HMX (run 5) whereas nitromethane alone (run 3) produced results similar to those shown in Table 3.

Although initially promising, sequential recrystallizations from nitromethane/cyclohexanone mixtures (Table 4, runs 6 and 7) yielded no advantage over pure nitromethane. The overall yields are low and the purity still below 98%. Thus the process of complexation and recrystallization is not appropriate for the purification of SEX.

#### Hot Column Chromatography

Although adequate separation of DADN, SEX and HMX is obtained on TLC plates, column chromatographic separation is hampered by the low solubility of the mixture. To overcome this problem, we attempted hot column chromatographic separation of DADN/SEX/HMX mixtures. Table 5 shows the results of several hot column chromatographic trials. The column temperature was maintained by a hot water jacket in runs 1 through 3. Run 1 (elution temperature 65°C) yielded small quantities of SEX (88 to 94% purity as determined by analytical HPLC) containing HMX as the sole contaminant. These products were obtained by allowing



Table 4  
RECRYSTALLIZATION OF IMPURE SEX WITH PRESUMED COMPLEXATION OF HMX

| Run                   | Starting Material <sup>a</sup> |      |     |     | Solvents                          | ml           | Recovery<br>(g) | Yield<br>(g) | Ratio of Products<br>Recovered <sup>a</sup> |          |          |
|-----------------------|--------------------------------|------|-----|-----|-----------------------------------|--------------|-----------------|--------------|---|----------|----------|
|                       | (g)                            | DADN | SEX | HMX |                                   |              |                 |              | DADN  | SEX      | HMX      |
| 1                     | 1.0                            | 14   | 44  | 42  | Nitromethane<br>Cyclohexanone     | 25<br>5      | 0.70            | 70.0         | 19.6  | 47.6     | 32.8     |
| 2                     | 1.0                            | 5    | 65  | 30  | Nitromethane<br>Cyclohexanone     | 30<br>10     | 0.58            | 58.0         | 9   | 62       | 29       |
| 3                     | 0.75                           | -    | 58  | 42  | Nitromethane                      | 11           | 0.60            | 80.0         | -   | 66.1     | 33.9     |
| 4                     | 0.75                           | -    | 58  | 42  | Nitromethane<br>Cyclohexanone     | 5<br>5       | 0.51            | 68.0         | -   | 93.3     | 6.7      |
| 5                     | 0.75                           | -    | 58  | 42  | Nitromethane<br>Dimethylformamide | 2.5<br>2.5   | 0.60            | 80.0         | -   | 37.0     | 63.0     |
| 6-1                   | 3.3                            | -    | 49  | 51  | Nitromethane<br>Cyclohexanone     | 15           | 2.45            | 74.2         | -   | 66(60.8) | 33(39.2) |
| -2                    | 2.45                           | -    | 66  | 33  | Nitromethane<br>Cyclohexanone     | 12.5<br>12.5 | 1.82            | 74.2         | -   | 77(70.4) | 23(29.6) |
| -3                    | 1.82                           | -    | 77  | 23  | Nitromethane<br>Cyclohexanone     | 7.5<br>7.5   | 1.45            | 79.6         | -   | 90       | 10       |
| -4                    | 1.45                           | -    | 90  | 10  | Nitromethane<br>Cyclohexanone     | 7.5<br>7.5   | 1.10            | 75.8         | -   | 92(87)   | 8(13)    |
| -5                    | 1.10                           | -    | 92  | 8   | Nitromethane<br>Cyclohexanone     | 12.5<br>12.5 | 0.85            | 77.2         | -   | 95(93)   | 5(7.0)   |
| Overall % yield: 25.7 |                                |      |     |     |                                   |              |                 |              |   |          |          |
| 7-1                   | 3.3                            | -    | 49  | 51  | Nitromethane<br>Cyclohexanone     | 10<br>20     | 2.50            | 75.7         | -   | 58(59)   | 42(41)   |
| -2                    | 2.50                           | -    | 58  | 42  | Nitromethane<br>Cyclohexanone     | 7<br>14      | 1.90            | 76.0         | -   | 70(70)   | 30(30)   |
| -3                    | 1.90                           | -    | 70  | 30  | Nitromethane<br>Cyclohexanone     | 5<br>10      | 1.38            | 72.6         | -   | 83       | 17       |
| -4                    | 1.38                           | -    | 83  | 17  | Nitromethane<br>Cyclohexanone     | 5<br>10      | 1.15            | 83.3         | -   | 92(84)   | 8(16)    |
| -5                    | 1.15                           | -    | 92  | 8   | Nitromethane<br>Cyclohexanone     | 8<br>16      | 0.83            | 72.1         | -   | 93(93)   | 7(7)     |
| Overall % yield: 25.1 |                                |      |     |     |                                   |              |                 |              |   |          |          |

<sup>a</sup>Composition determined by proton NMR; analytical HPLC compositions in parenthesis.

Table 5  
HOT CHROMATOGRAPHIC SEPARATION OF DADN/SEX/HMX

| Run | Starting Material <sup>a</sup> |      |     |     | Nitromethane <sup>b</sup><br>(ml) | Column<br>Temp.<br>(°C) | Silica<br>gel<br>(g) | Fraction<br>Number | Ratio of<br>Product Recovered |      |      |
|-----|--------------------------------|------|-----|-----|-----------------------------------|-------------------------|----------------------|--------------------|-------------------------------|------|------|
|     | wt<br>(g)                      | DADN | SEX | HMX |                                   |                         |                      |                    | (g)                           | SEX  | HMX  |
| 1   | 3.7                            | 12   | 59  | 33  | 80                                | 65                      | 225                  | 4                  | Trace                         | 88.6 | 11.6 |
|     |                                |      |     |     |                                   |                         |                      | 5                  | Trace                         | 91.0 | 9.0  |
|     |                                |      |     |     |                                   |                         |                      | 6                  | Trace                         | 93.6 | 6.4  |
| 2   | 1.5                            | 5    | 65  | 30  | 40                                | 70                      | 228                  | 3-6                | 0.075                         | 99.9 | -    |
| 3   | 1.5                            | 5    | 65  | 30  | 40                                | 70                      | 210                  | 7                  | Trace                         | 98.5 | 1.5  |
|     |                                |      |     |     |                                   |                         |                      | 8-14               | 0.44                          | 99.8 | 0.2  |
| 4   | 8.3                            | 3    | 40  | 57  | 150                               | 95-100                  | 600                  | 6-9                | 3.7                           | 61   | 39   |
|     |                                |      |     |     |                                   |                         |                      | 10-15              | 0.87                          | 90   | 10   |
| 5   | 6.5                            | 23   | 55  | 22  | 175                               | 90-95                   | 600                  | 1-7                | 0.64                          | -    | 100  |
|     |                                |      |     |     |                                   |                         |                      | 10-13              | 2.41                          | 42.2 | 57.8 |
|     |                                |      |     |     |                                   |                         |                      | 14-15              | 1.12                          | 100  | -    |
|     |                                |      |     |     |                                   |                         |                      | 16-18              | 0.42                          | 100  | -    |
| 6   | 16                             | 18   | 41  | 41  | 400                               | 90-95                   | 600                  | 1-6                | 2.51                          | -    | 100  |
|     |                                |      |     |     |                                   |                         |                      | 6-13               | 9.91                          | 57.8 | 42.2 |
|     |                                |      |     |     |                                   |                         |                      | 14-19              | 2.50                          | 95   | 5    |
| 7   | 15                             | 17   | 45  | 38  | 400                               | 90-100                  | 600                  | 1-6                | 2.10                          | -    | 100  |
|     |                                |      |     |     |                                   |                         |                      | 7-12               | 7.33                          | 60   | 40   |
|     |                                |      |     |     |                                   |                         |                      | 13-16              | 2.95                          | 95   | 5    |
|     |                                |      |     |     |                                   |                         |                      | 17-23              | 1.55                          | 97   | 3    |

<sup>a</sup>Composition determined by proton NMR and/or analytical HPLC.

<sup>b</sup>Nitromethane required to dissolve starting material.

the fractions collected to stand overnight, during which time slight evaporation of the solvent preferentially precipitated SEX from solution. The DADN was completely retained on the silica gel; however, prolonged elution with 70°C nitromethane finally yielded DADN. The temperature of the column and solvent reservoir was raised slightly (70°C) to increase the solubility of the crude HMX/SEX/DADN mixture. In runs 2 and 3, 1.5 g of the mixture (30:65:5 ratio HMX/SEX/DADN as determined by proton NMR) yielded 0.44 g of 99.8% SEX. The residual impurity proved to be HMX, with DADN remaining on the column. The observation that hot column chromatography on silica gel separated DADN from HMX/SEX/DADN mixtures prompted the use of silica-gel hot plug filtration, runs 4 and 5, as a quick method for removal of DADN. The temperature was maintained between 90° and 100°C by running steam through the system. All the DADN was retained on the silica gel in both runs. Thus, rapid separation of small quantities of DADN (5 to 20%) can be accomplished by hot plug filtration. Furthermore, the hot plug filtration partially separates HMX and SEX. The process is only limited by the solubility of the crude mixtures in hot nitromethane.

#### Preparative HPLC

After the SEX/HMX mixture is obtained from the hot column chromatography, it is purified to 98+% SEX by preparative HPLC. Again, the only limitation is the solubility of the SEX/HMX in nitromethane. However, since nitromethane is used in the hot column, the eluted SEX/HMX mixture can be applied directly to the HPLC without further handling. Commercially available, prepacked silica-gel columns were used to effect separation. Thus, a SEX/HMX mixture with a solubility of approximately 1.0 g per 50 to 100 ml of nitromethane afforded 99.9+% SEX. Samples of 1 to 2 grams can be purified per injection, with a retention time of 15 minutes.

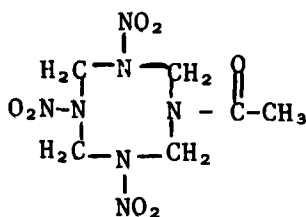
Although the purification of a 4-kilogram quantity of SEX by this method would be prohibitively expensive, quantities up to one kilogram are conceivable. Further, we are currently in contact with Waters and Associates to see if our preparative HPLC can be automated. This would

allow for continuous operation and substantially lower the cost of  
purifying SEX in multigram quantities. Even if a new machine had to  
be purchased, at government expense, the resulting savings in time and  
labor would far exceed this initial investment. Thus, if automation is  
possible, separation of DADN from the crude DADN/SEX/HMX by hot column  
chromatography, followed by preparative HPLC separation of SEX/HMX,  
will afford SEX in greater than 98+% purity, and at a reasonable cost.

## CHARACTERIZATION OF SEX

SEX appears sufficiently stable in normal nitrolysis media to exist as a contaminant in RDX/HMX manufacturing process. The characteristics of SEX are as follows:

Structural Formula:



Empirical Formula:  $C_6H_{11}N_7O_7$

Elemental Analysis: Calculated: C, 24.57; H, 3.75; N, 33.45  
Found: C, 24.21; H, 3.76; N, 33.45

Melting Point: 237-237.5°C

Molecular Weight: 293 (Calculated)

Solubility: Soluble in dimethylsulfoxide. Slightly soluble in acetone, nitromethane and acetonitrile. Almost insoluble in ethanol, benzene and ether.

Impact Sensitivity (drop weight test)--Greater than 300 kg-cm compared with 148 kg-cm for pure HMX. SEX is sensitive to direct strong hammer blows. During our investigations SEX has exhibited no instability, but because of the hammer results should be handled as a potential explosive, like HMX.

Infrared Spectrum: See Figure 2.

Proton NMR Spectrum: See Figure 3.

Chemical Properties<sup>4</sup>--SEX gives a positive Franchimont nitramine reaction, but a negative Liebermann nitroso test. Decomposition in hydroxide fails to produce free  $CH_3COO^-$  for a lanthanum nitrate test.

However, if SEX is decomposed in 96% sulfuric acid, the distillate gives a lanthanum nitrate test.

SEX appears inert to boiling acetic anhydride and unaffected by treatment with ammonium nitrate-nitric acid mixtures. Absolute nitric acid at 50°-60°C converts SEX to HMX. Warm 70% nitric acid destroys the compound rapidly, as does 10% aqueous sodium hydroxide and 28% ammonia.

Purity--The purity of SEX was determined by analytical HPLC with a Spectra-Physics 3500B Liquid Chromatograph. A Waters RCM-100, C<sub>18</sub> cartridge with a mobile phase of 80/20 water/methanol was used for DADN/SEX/HMX mixtures. An internal standard of RDX was used with  $1/R_f^*$  values of 1.5 for HMX, 1.5 for SEX, and 1.7 for DADN. Hot-column chromatographed SEX contained no detectable amounts of DADN (starting material) and only 1 to 2% HMX (sole contaminant). High-pressure liquid chromatographed material contained no DADN or HMX. Also, no other contaminants were detected by analytical HPLC, ensuring a 99.9+% purity of SEX.

---

\*  $R_f$  = response factor.

NO. 007-1493

PERKIN-ELMER

|   |                                    |                                |                                 |   |
|---|------------------------------------|--------------------------------|---------------------------------|---|
| CONCENTRATION <u>5 mg SEX/ 500 mg KBr</u> | SCAN MODE                          | ACCY. <input type="checkbox"/> | SURVEY <input type="checkbox"/> | SPECTRUM NO. <u>IR-11784-10-1</u>               |
| THICKNESS _____                           | HI ENERGY <input type="checkbox"/> | CAL. <input type="checkbox"/>  |                                 | SAMPLE <u>1-Acetyloctahydro-3,5,7-trinitro-</u> |
| PHASE <u>KBr Pellet</u>                   | RESOLUTION <u>20</u>               |                                |                                 | <u>1,3,5,7-tetrazocine (SEX)</u>                |
| REMARKS <u>99.9% SEX</u>                  | OPERATOR _____                     | C.D.B. _____                   | DATE <u>9-16-80</u>             | ORIGIN <u>Recrystallized from CH NO. 3</u>      |

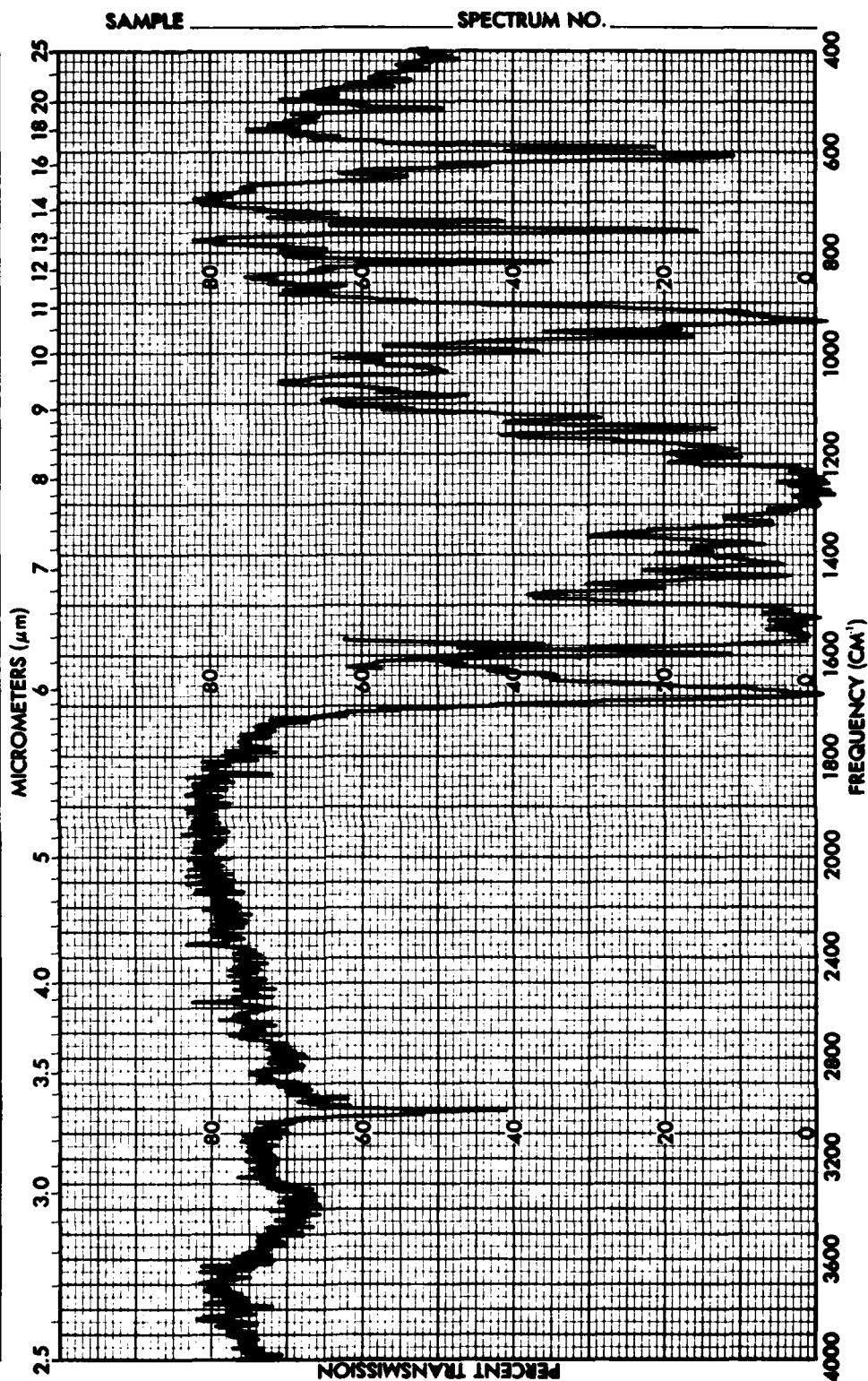


FIGURE 2. INFRARED SPECTRUM

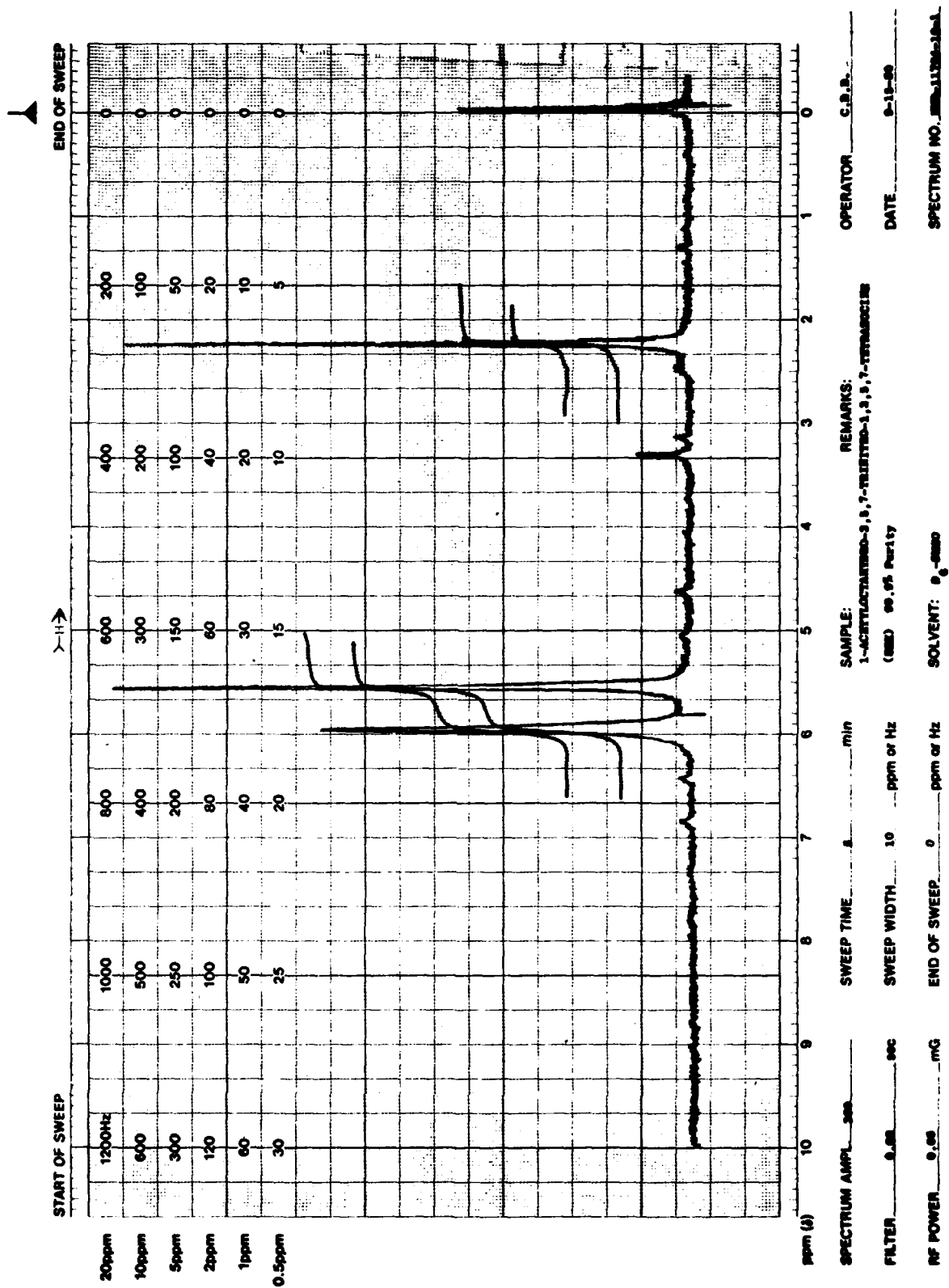


FIGURE 3. NMR SPECTRUM



## EXPERIMENTAL PROCEDURE

Optimum Batch Conditions for the Preparation of 1-Acetyloctahydro-3,5,7-trinitro-1,3,5,7-Tetrazocine (SEX)--DADN (40.0 g, 0.138 mole) was dissolved in 266 ml of 100%  $\text{HNO}_3$  at 20°C. With cooling (ice/water bath), 75 ml of trifluoroacetic anhydride was added at such a rate that the temperature of the mixture remained between 15°C and 20°C. At the end of the addition, the flask was placed in an oil bath preheated to 40°C and stirred for 60 min at this temperature. The mixture was then poured into ice/water and stirred for 30 min, which precipitated the crude SEX. The precipitate was filtered, washed with several large portions of water, and dried over  $\text{P}_2\text{O}_5$  in vacuo, yielding 33.7 g (84%) crude SEX. Proton NMR analysis of the product indicated the following composition: 18% DADN, 41% SEX, 41% HMX. Analytical HPLC of the product indicated the following composition: 20% DADN, 49% SEX, 31% HMX.

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#### LIST OF PERSONNEL RECEIVING CONTRACT SUPPORT

The following persons received support under contract #DAMD17-80-C-0013.

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